SCIENCE FOR CERAMIC PRODUCTION

SYNTHESIS OF IRON ALUMINATES AND A NEW MODIFICATION OF ALUMINUM OXIDE UNDER SHOCK WAVES FROM EXPLOSIVES (REVIEW)

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The results of an x-ray diffraction investigation of iron aluminate with unit cell parameter $a = 8.090(4)$ Å, cation-defective iron aluminate $Fe_{0.5}Al_{2.23}O_4$ with $a = 8.002$ Å, and a new modification of aluminum oxide synthesized under shock waves from explosives containing aluminum are presented. Aluminum oxide can crystallize in the hexagonal system in a primitive lattice with $a = 9.151(1)$ Å, $c = 7.945(2)$ Å, $V = 576$ Å^3 or in a tetragonal system in a primitive lattice with one-half the volume — $a = 7.941(2)$ Å, $c = 4.575(1)$ Å, $V = 288$ Å^3.

In our previous works [1 – 3], we were able to synthesize by shock-wave and explosive methods aluminum oxide $Al_{8/3}O_4$ with the unit cell parameters $a = 7.935(1)$ and $7.953(3)$ Å [1, 2] with structure different from γ-$Al_{8/3}O_4$ and cation-defective spinel $Al_{0.67}\square_{33}[Al]_2O_4$ with $a = 7.905$ Å [4]. The unit cell parameter of the $Al_{8/3}O_4$ crystals synthesized in [2] is essentially equal to the parameter a (7.948 Å) of σ-Al_2O_3 crystals grown from melt [5].

Investigation of σ-Al_2O_3 crystals has shown that the cationic distribution and the structure correspond to the crystal-chemical formula $Al[Al_{5/3}\square_{1/3}]O_4 - Al_{2.667}O_4$. The interplanar distances of the synthesized aluminum oxide in [2] are essentially identical to those of σ-Al_2O_3, but the intensity of lines with $hkl = 422$, 511, and 440 are not always the same as the intensities of the lines of σ-Al_2O_3 for the same values hkl. This indicated that a phase with a structure different from that of σ-Al_2O_3 was synthesized in [1, 2].
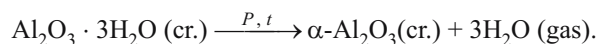
Explosive synthesis of aluminum oxide [3] was conducted in a specially constructed 200 cm^3 vessel, made of 12Kh18N10T steel, of a small explosive calorimeter under vacuum. The residual air pressure was 3 – 5 mm Hg. The initiator was a 0.1 g lead azide charge.

In [6] iron aluminate $FeAl_2O_4$ (hercynite) with $a = 8.140(2)$ Å was synthesized under a shock wave acting with axisymmetric loadi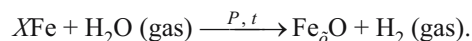ng on gibbsite $Al(OH)_3$ placed in a steel storage ampul. Shock-wave loading was achieved by a sliding detonation wave from the explosion of a cast charge of trotyl-hexogen 40/60 with density 1.672 gm/cm^3, placed in a steel shell. The detonation velocity was 8100 m/sec and the detonation pressure was 26 GPa.

Initially, an ampul with the standard construction, which for axisymmetric shock-wave loading is placed along the axis of explosive charge, was used. Under the experimental conditions the ampul was destroyed by the explosion of $Al_2O_3 \cdot 3H_2O$. The construction of the ampul was improved, and its walls were capable of withstanding an explosion of $Al_2O_3 \cdot 3H_2O$ without collapsing [6].

Iron aluminate $FeAl_2O_4$ was formed in [6], evidently, as a result of the interaction under high pressure and temperature of the products of decomposition of aluminum hydroxide with the steel wall of the ampul.

$$Al_2O_3 \cdot 3H_2O \text{ (cr.)} \xrightarrow{P, t} \alpha\text{-}Al_2O_3(\text{cr.}) + 3H_2O \text{ (gas)}.$$

The most likely product of interaction of water vapor with the ampul material is wüstite Fe_xO:

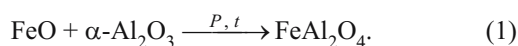$$X Fe + H_2O \text{ (gas)} \xrightarrow{P, t} Fe_\delta O + H_2 \text{ (gas)}.$$

Wüstite crystallizes in a structure of the type NaCl. At atmospheric pressure wüstite is nonstoichiometric: it always contains cationic vacancies, and some Fe^{2+} ions are replaced by Fe^{3+}. The unit cell parameter a depends on the degree of defectiveness. This oxide forms with low oxygen partial
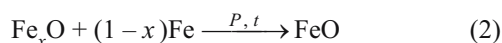
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pressures and is stable at temperatures above 570°C. At 570°C its composition is $Fe_{0.938}O$, and at lower temperatures Fe_xO decomposes into iron and magnetite Fe_3O_4. As temperature increases, the region of homogeneity increases to $Fe_{0.95}O – Fe_{0.80}O$ [7]. The chemical activity of Fe_xO depends on the degree of defectiveness of the structure. Hydrogen at temperatures 500 – 600°C reduces wüstite to metallic iron. Carbon and carbon monoxide CO have the same effect. Water vapor can oxidize to Fe_2O_3. Stoichiometric FeO forms in 1 h from $Fe_{0.95}O$ and metallic iron under pressures 3.6 – 5.3 GPa and temperature 770°C with lattice parameter $a = 4.323$ Å, which is somewhat larger than for the nonstoichiometric phase (4.306 – 4.320 Å) [8].
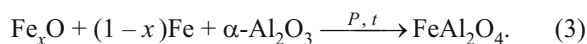
The results of an x-ray diffraction investigation of the products formed with shock-wave loading on gibbsite placed in a steel ampul suggests that hercynite ultimately formed as a result of the interaction of corundum with würstite, whose composition is close to stoichiometric:

$$FeO + \alpha\text{-}Al_2O_3 \xrightarrow{P,\,t} FeAl_2O_4. \qquad (1)$$

Stoichiometric wüstite evidently appeared as a result of a reaction previously presented in [8]:

$$Fe_xO + (1 - x)Fe \xrightarrow{P,\,t} FeO \qquad (2)$$

or

$$Fe_xO + (1 - x)Fe + \alpha\text{-}Al_2O_3 \xrightarrow{P,\,t} FeAl_2O_4. \qquad (3)$$

According to the results of [9, 10], the reaction (3) is accompanied by a decrease of the Gibbs energy. The thermodynamic parameters of the reaction (1) were obtained in [9] by the emf method with a solid electrolyte:
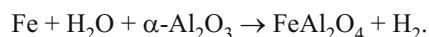
$$\Delta H_{298}^0 = -10.8 \text{ kcal/mole } (-45.2 \text{ kJ/mole});$$

$$\Delta G_{298}^0 = -9.6 \text{ kcal/mole } (-40.2 \text{ kJ/mole}).$$

The change in the Gibbs energy with increasing temperature is described by the equation [10]:

$$\Delta G^0 = -7918 + 1.46T \ (\pm 1200 \text{ cal}).$$

The processes arising in a steel ampul with gibbsite under a shock wave are described by the resulting reaction:

$$Fe + H_2O + \alpha\text{-}Al_2O_3 \rightarrow FeAl_2O_4 + H_2.$$

The change in the Gibbs energy for this reaction with increasing temperature is given by the equation [10]:

$$\Delta G^0 = -5850 + 0.37T.$$

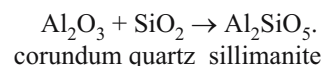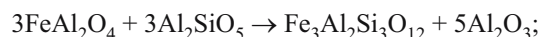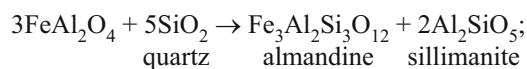The thermodynamic functions for the reaction forming hercynite from the elements

$$Fe + 2Al + 2O_2 \rightarrow FeAl_2O_4 \qquad (4)$$

were determined in [9]: $\Delta H_{298}^0 = -474$ kcal /mole (-1983 kJ /mole), $\Delta G_{298}^0 = -446.8$ kcal/mole (-1869.4 kJ/mole).

In [9] $FeAl_2O_4$ is one of the phases of the left-hand electrode of a galvanic cell. Hercynite was obtained during prolonged calcination at temperature 1000 – 1100°C in a sealed evacuated quartz ampul of a carefully mixed and pressed mixture of powdered $1/3(Fe + Fe_2O_3) + \alpha\text{-}Al_2O_3$.

Diffusion processes and systems containing chromite and iron-group aluminates, and the reaction forming these compounds from oxides at high temperatures proceed very slowly. The extremely high rate of synthesis of hercynite in [6], complicated by the initial heterogeneity of the experimental conditions, is evidently explained by the possibility of achieving a high temperature (hercynite melts congruently at 1780°C) and by intense hydrodynamic mixing of the reacting substances in the reaction zone under the action of a strong shock wave. After the ampul was opened, it became obvious that the transformation products are compacted and arranged in a ring on the walls of the through channel with a diameter of 1 mm, which appeared along the axis of the ampul.

In nature, iron aluminate $FeAl_2O_4$ (hercynite) is rarely encountered and is abundant in rocks with a high degree of metamorphism. It forms associations with andulasite $Al_2[SiO_4]O$, sillimanite $Al(AlSiO_5)$, and garnet $Fe_3Al_2Si_3O_{12}$ (almandine). The geological process leading to the formation of the minerals probably occurs as a result of the following reactions [11]:

$$3FeAl_2O_4 + 5SiO_2 \rightarrow Fe_3Al_2Si_3O_{12} + 2Al_2SiO_5;$$
$$\quad \text{quartz} \qquad \text{almandine} \qquad \text{sillimanite}$$

$$3FeAl_2O_4 + 3Al_2SiO_5 \rightarrow Fe_3Al_2Si_3O_{12} + 5Al_2O_3;$$

$$Al_2O_3 + SiO_2 \rightarrow Al_2SiO_5.$$
$$\text{corundum quartz sillimanite}$$

Hercynite belongs to a class of compounds with spinel structure, which is described by the Fedorov symmetry group $Fd3m$. The unit cell of spinel contains 32 oxygen atoms with almost undistorted close packing. For every 32 oxygen atoms there are 64 tetrahedral and 32 octahedral voids. The tetrahedral voids correspond to structurally equivalent positions $8(a)\,A$, $8(b)\,A^*$, $48(f)\,A^{**}$ and 32 octahedral positions $16(d)\,B$, $16(c)\,B^*$. The oxygen ions forming cubic close packing occupy the monovariant position $32(e)$; x, x, x.

The most important representatives of the spinel structure are compounds with the general formula $A[B]_2X_4$ (the letter in brackets denotes a cation in octahedral positions B). If X is oxygen and A is a bivalent cation, then this formula describes the structure of normal spinel. Normal spinels are compounds where A = Mg, Mn, Co, Ni, Zn, Cu and B = Al, Cr, and Fe as well as minerals — chromite $(Mg, Fe)[Cr]_2O_4$, franklinite $Zn[Fe]_2O_4$, and hercynite $Fe[Al]_2O_4$. The precious spinel $MgAl_2O_4$ under natural conditions is close to normal [12]. The mineral ceylonite is a spinel with intermediate composition between the precious spinel and hercynite. The formation of this mineral is largely associated with per-

fect isovalent isomorphism of the ions Mg^{2+} (0.72 Å) and Fe^{2+} (0.78 Å), which has been studied in detail in natural silicates and borates: olivines, pyroxenes, biotites, ludwigites, vonsenites, and also spinels — ferrites and the artificial system $MgO - FeO$ [13].

There are many compounds with a structure close to that of spinel but with tetragonal or rhombic distortion of the cubic symmetry. The distortion is due to the nature of the cation and is most often observed at low temperatures.

If a trivalent cation occupies a tetrahedral position, then the spinel is said to be inverted $B[AB]X_4$. Natural iron ferrite (magnetite) and the mineral trevorite $NiFe_2O_4$ are examples of inverted spinels $Fe^{3+}[Fe^{2+}Fe^{3+}]O_4$ and $Fe^{3+}[Ni^{2+}Fe^{3+}]O_4$.

Magnetite and nickel ferrite are ferritic magnets whose theory was developed by L. Néel. According to his theory, the ions in the positions A and B of the structure possess oppositely directed magnetizations. The Fe^{3+} ions do not contribute to the total magnetization of the Fe_3O_4 phase: the spin moments of the eight Fe^{3+} ions, occupying tetrahedral positions, are oppositely directed to the eight Fe^{3+} ions occupying octahedral positions, and as a result compensate one another. The spin moments of the eight Fe^{2+} ions are oriented in the same direction and give the total magnetization. For the same reason, the total magnetic moment in nickel ferrite is due to the presence in it of ions of nickel which has two unpaired electrons.

Many spinels are characterized by intermediate degrees of inversion x: $A_{1-x}B_x[A_xB_{2-x}]O_4$. The quantity x depends on the composition and temperature. The degree of inversion x in magnesioferrite $MgFe_2O_4$ can vary over wide limits. At high temperatures $x = 0.67$ and the distribution becomes statistical. In $NiMn_2O_4$ the degree of inversion x varies from 0.37 (quenching) to 0.47 (slow cooling).

There is still no rigorous theoretical validation of intracrystalline ionic exchange in solid solutions and spinels. Many theories substantially exaggerate the stability of normal spinel.

Hercynite at temperatures above 875°C forms a solid solutions with magnetite [14 – 20] and, just like $MgAl_2O_4$ [12], with aluminum oxide (Fig. 1) [14].

The synthesis of hercynite with $a = 8.125$ Å and the solid solutions of $FeAl_2O_4$ with magnetite Fe_3O_4 and Al_2O_3 are described in detail in [14]. In this work $FeAl_2O_4$ was synthesized by heating mixtures of FeO and Al_2O_3 in an argon atmosphere in the temperature range 600 – 1800°C, and phases with variable composition were synthesized by heating mixtures of FeO, Fe_2O_3, and Al_2O_3 in air at temperatures 1400 – 1600°C. The lattice parameters a of $FeAl_2O_4$ samples obtained at different temperatures depend on the synthesis temperature. The parameter a changes most notably in the temperature range 1500 – 1800°C — it decreases with increasing temperature of spinel synthesis. In [14] limited miscibility of the components was found in the system $FeAl_2O_4 - Al_2O_3$ (3.0 – 21.2% Al_2O_3, molar content). The solubility of Al_2O_3 increases sharply in the presence of Fe^{3+}
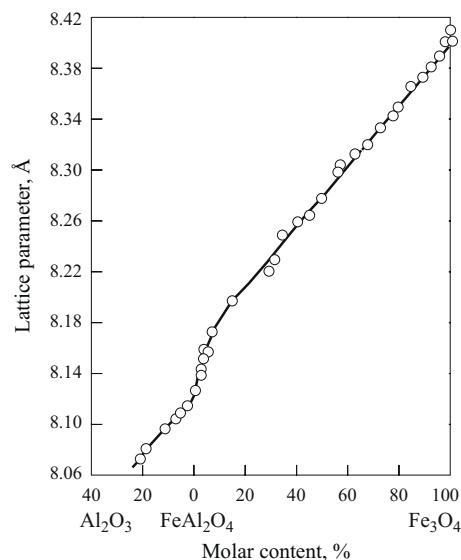

Fig. 1. Unit cell parameter of the spinel phase versus the content of magnetite and aluminum oxide.

ions. The entry of Al^{3+} ions into the hercynite lattice decreases the unit cell parameter a:

Al_2O_3 molar content in hercynite	Unit cell parameter a, Å
3.0	8.115
6.1	8.111
7.0	8.105
11.2.	8.097
19.9	8.081
21.2	8.072

The composition of the spinel phase in the system $Fe_3O_4 - FeAl_2O_4$ was determined in [16] by the x-ray diffraction method — according to the shift of the reflections (333) and (440). According to the data in this work, the unit cell parameter a changes for magnetite from 8.391 ± 0.002 Å and for hercynite up to 8.150 ± 0.004 Å according to the equation: $a = 8.391 - 0.00190X - 0.5X^2 \times 10^{-5}$ (X is the molar content hercynite in the solid solution).

The unit cell parameter a for hercynite synthesized in [15] from FeO and Al_2O_3 at temperatures 1000 – 1250°C in a helium atmosphere in a period of 2 days is 8.152 Å.

In [17] the Mössbauer spectra of a series of samples of the system $Fe_{3-x}Al_xO_4$, $0 \le x \le 1.5$, were investigated at room temperature. The Mössbauer spectrum of the sample with $x = 0$ consists of two overlapping sextuplets, one of which is ascribed to Fe^{3+} ions occupying tetrahedral positions (A) and the other to the ions Fe^{2+} and Fe^{3+} occupying octahedral (B) positions. The Mössbauer spectrum of samples with $x = 0.05$, 0.1, and 0.3 also consists of two sextuplets. However, the lines of the spectrum which belong to iron ions occupying the B positions are broadened. The broadening of the lines of Fe^{2+} and Fe^{3+} ions in the B posi-

tions is due to the effective charges of the Al^{3+} ions entering the B positions of the lattice. Additional lines associated with a transition of Fe^{2+} ions from B into A positions appear in the Mössbauer spectrum of the sample with $x = 0.6$. The Mössbauer spectrum of samples with $x = 0.9$, 1.2, and 1.5 and for $x \leq 1$ does not fit within the framework of conventional Zeeman splitting. The results of [17] agree with the data presented in [18] on the magnetic properties of the solid solutions $Fe_3O_4 - FeAl_2O_4$.

The authors of [18] established that in a wide range of concentrations the magnetic moment of the solid solution $Fe_{3-x}Al_xO_4$ follows the law $\mu = 4 - 3X$ (X is the number of Al^{3+} ions replacing Fe^{3+} per $Fe_{3-x}Al_xO_4$ molecule). As the Al^{3+} content increases, the Curie temperature (the spontaneous magnetization vanishes above this temperature) decreases, and it is close to 0 K for the composition $FeAl_2O_4$. Analysis of the temperature dependence of the magnetization of $Fe_{1-x}Al_xO_4$ showed that the compensation point ($\mu = 0$) lies between $X = 1.14$ and 1.51.

L. Néel's theory explains the results of [18] presented above, if it is assumed that when an Al^{3+} ion replaces a Fe^{3+} ion the Fe^{2+} ions move from octahedral into tetrahedral positions. As a result, the direction of the magnetic moments of these Fe^{2+} ions reverses. According to the data of [18], the distribution of cations in the structure of the iron aluminate is described by the formula $Fe_{1-x}^{3+}[Fe_{1-x}^{2+}Fe^{3+}Al_x]O_4$ for $x \leq 1$ and $Fe^{2+}[Fe_{2-x}^{3+}Al_x^{3+}]O_4$ for $1 < x \leq 2$. As the content of Al^{3+} ions increases, spinel changes from inverted to normal.

The constants of the cation distribution and the concentration of lattice defects in $Fe_{3-x}Al_xO_4$ were calculated on the basis of the proposed models and experimental data on the position of the phase boundary $Fe_3O_4 - FeAl_2O_4$ [16, 19] at temperatures 1500 and 1280°C in [20]. The authors of [20] concluded that the cations Al^{3+} mainly occupying octahedral positions and the enthalpy of their distribution is temperature independent. The octahedral positions at low temperatures were found to be preferable for Fe^{2+} cations as compared with Fe^{3+} cations. As temperature increases, the distribution of the cations Fe^{2+} and Fe^{3+} between tetrahedral and octahedral positions approaches the statistical distribution.

The enthalpies (ΔH^0, kJ/mole) of the preference of Al^{3+}, Fe^{2+}, and Fe^{3+} ions for octahedral positions in an oxygen as compared with tetrahedral positions are [21]: $\Delta H^0(Al^{3+}) = -44.4$, $\Delta H^0(Fe^{2+}) = -26.4$, $\Delta H^0(Fe^{3+}) = -22.2$. These data agree with the results of [20].

The structure of synthetic hercynite has been investigated in [22] by Ritveld's method (full-profile analysis of powder diffraction data). The unit cell parameter a at 20°C is 8.15579(6) Å. The oxygen coordinates $x(O) = 0.2633(2)$. Annealing at 850°C results in cationic disorder in the structure with the inversion parameter $x = 0.163(5)$. According to the data of [11], at 900°C the inversion parameter increases to $x = 0.18$.

In [23] crystals of normal spinel $FeAl_2O_4$ were synthesized (I) hydrothermally (2 kbar, 700°C, 16 h) and (II) by calcination of α-Al_2O_3 and Fe_2O_3 at high temperature (1400°C for 5 h) in a controllable atmosphere of the gases $CO_2 : (CO + CO_2) = 10\%$ followed by quenching in the same atmosphere. Subsequently these samples I and II were calcined at 500°C for 112 h (I) and 262 h (II) in sealed evacuated quartz ampuls. Cooling was conducted in air. The degree of inversion as a result of these calcinations $x = 0.101$ ($Fe_{0.899}Al_{0.101}$)$[Al_{1.899}Fe_{0.101}]O_4$. Next, repeated sintering at 900°C for 16 h and quenching were performed. Then these samples were quenched.

X-ray diffraction and Mössbauer spectroscopy, just as in [11, 22], showed a regular increase of the cationic disorder with increasing temperature. According to the x-ray data, the inversion parameter x increased from 0.101 at 500°C to 0.187 at 900°C ($Fe_{0.813}Al_{0.187}$)$[Al_{1.813}Fe_{0.187}]O_4$, and according to Mössbauer spectroscopy $x = 0.162$ at 500°C and 0.19 at 900°C. The increase in the inversion parameter is accompanied by a smooth decrease of the parameter U characterizing the position of oxygen in the structure and a decrease of the unit cell parameter a. Quenching of intracrystalline cationic disorder in the structure of hercynite at temperatures above 900°C was found to be impossible. In the opinion of the authors of [23], this is explained by the increase in the diffusion rates of the cations which are due to the presence of cationic vacancies. The vacancy defects Fe^{3+} easily arise in this spinel because of partial extremely rapid oxidation of the cations Fe^{2+} into Fe^{3+} at high temperatures.

According to the data in [24], the degree of inversion in hercynite can reach $0.23 - 0.25$. These data were obtained using the Mössbauer effect and powder x-ray diffraction. The Debye – Scherrer method with a chamber with effective diameter 140 mm and MoK_α radiation were used. One of the main drawbacks of this chamber, as well as other chambers with photographic recording of x-ray radiation, are the inaccuracy of the values of the line intensities and the resolving power.

The cationic distribution in hercynite $Fe_{1-x}Al_x[Fe_xAl_{2-x}]O_4$ was investigated on two samples. One sample was synthesized from a preprepared solid solution of $Fe_{0.5}Al_{1.5}O_3$ and Fe, taken in the molar ratio 4 : 1. The second sample was prepared from a mixture of Fe_2O_3, Al_2O_3, and Fe powders, taken in the molar ratio of 1 : 3 : 1. Both samples in the form of pellets were calcined in an atmosphere of H_2 and CO_2 (1 : 1) at 1300°C for 4 h, and then at 1000°C in a sealed evacuated quartz ampul. Cooling to room temperature was performed at the rate 30 K/h. The x-ray diffraction pattern was indexed in the spinel lettuce with $a = 8.096$ Å. The Mössbauer absorption spectrum showed that some Fe^{2+} ions were in the B positions and others in the A positions.

The degree of inversion x of spinel, as determined from the relative integral intensities of the lines in Mössbauer

spectrum, was found to be 0.23. According to the x-ray data, $x = 0.25$.

The cationic-defective spinel with the composition $Fe_{0.5}Al_{2.33}O_4$ and unit cell parameter $a = 8.00$ Å much shorter than in hercynite was found in [25]. This work presents two of the strongest lines of this phase — 2.83 and 2.41 Å with hkl 220 and 311, respectively. The authors of [25] believe that the phase $Fe_{0.5}Al_{2.33}O_4$ is one of the products of decomposition of hercynite in the temperature interval 900 – 1000°C at low oxygen pressure according to the reaction

$$7FeAl_2O_4 = 6Fe_{0.5}Al_{2.33}O_4 + 4Fe + 2O_2. \qquad (5)$$

It was established in [26] in a study of solid solutions of the system $ZnO – Al_2O_3$ that they have the spinel structure in the case of stoichiometric and nonstoichiometric compositions. Compositions close to Al_2O_3 possess a defect structure with vacancies in cationic positions. In [26] the structures were determined for the spinel $Zn_{0.99}Al_2O_4$ with $a = 8.088(1)$ Å and with cationic vacancies $Zn_{0.54}Al_{2.31}O_4$ with $a = 8.003(1)$ Å. For $Zn_{0.99}Al_2O_4$ the coordinates of the oxygen atoms $x(O) = 0.390$, $(Zn_{0.97}Al_{0.03})[Zn_{0.02}Al_{1.97}]O_4$, and the divergence factor $R = 0.046$. For $Zn_{0.54}Al_{2.31}O_4$ coordinates of the oxygen atom $x(O) = 0.385$, $(Zn_{0.53}Al_{0.46})[Zn_{0.01}Al_{1.85}]O_4$, and $R = 0.078$.

It should be noted that the content of Zn^{2+} and Al^{3+} ions is virtually the same as that of iron and aluminum ions in cation-defective iron aluminate $Fe_{0.5}Al_{2.33}O_4$.

In [27], two spinels were synthesized by shock-wave impact on amorphous aluminum hydroxide placed in a brass cylinder of a storage ampul: gahnite $ZnAl_2O_4$ with $a = 8.094$ Å and cation-defective (nonstoichiometric) spinel $Zn_{0.33}Al_{2.45}O_4$ with the same unit cell parameter as in the phase $Fe_{0.5}Al_{2.33}O_4$ [25]. The closeness of the compositions of these phases and the fact that the unit cell parameters are the same are probably explained by the small difference between the ionic radii of Zn^{2+} (0.74 Å) and Fe^{2+} (0.78 Å). Consequently, isovalent isomorphism of Zn^{2+} and Fe^{2+} is observed in ionic compounds and minerals; for example, in sphalerite [13]: (Zn, Fe)S.

In the series of the solid solutions of the system $ZnO – Al_2O_3$ which were studied it was established that the density decreases linearly and the unit cell parameter of spinel increases smoothly but nonlinearly as the aluminum oxide content increases (Fig. 2).

A method for synthesizing oxide phases has been described in our work: iron aluminates and a new modification of aluminum oxide with a structure that is derived from spinel. The method of excitation of an explosive transformation by means of an impact was used for the first time to synthesize these substances. The general idea of the mechanism of initiating an explosion by impact in solid explosives is given in [29].

Synthesis was performed in an apparatus (Fig. 3) consisting of a steel sleeve (carbon tool steel, GOST 1435) into
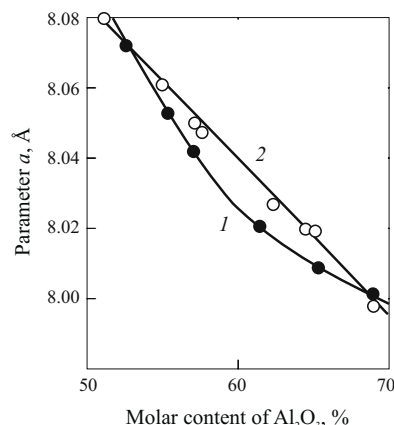

Fig. 2. Unit cell parameter of alumozinc spinel versus the aluminum oxide content. The curves *1* and *2* were constructed from the data in [26] and [28], respectively.
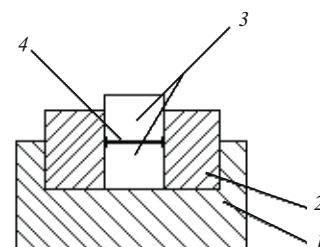

Fig. 3. Experimental setup: *1*) bottom; *2*) sleeve; *3*) rollers; *4*) explosive charge with aluminum.

which two cylindrical rollers, 10 mm in diameter and 11 mm long, made of ball bearing steel (GOST 801), were placed. The prepared 0.05 g charge of an explosive and aluminum (charge with bulk density 0.9 g/cm^3) were placed between the rollers. The composition of the explosive mixtures is presented in Table 1. The REAL program was used to calculate the temperature of the explosion. The computed pressure of the explosion in the experiments was 1.0 – 1.5 GPa.

The apparatus with the charge was placed on an anvil, a 10 kg mass was dropped on it from a height of 500 mm, and the presence or absence of an explosion was recorded. An explosion was taken to be an explosive transformation of the material accompanied by a sound effect, flame, or traces of burns on the rollers or sleeve of the apparatus.

TABLE 1.

Sample	Composition of explosive mixture, wt.%	Temperature, K	Number of experiments
1	Octogen/Al-90/10	3797	6
2	Octogen/Al-70/30	3838	3
3	Octogen/Al-80/20	4097	5
4	Desensitized hexogen/Al-80/20	4000	3
5	Octogen/Al-60/40	3868	3

TABLE 2.

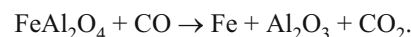| I	Iron aluminate		Aluminum oxide	
	d_e, Å	hkl	d_e, Å	hkl
52	2.8537	220	–	–
		220[*]		
27	–	–	2.8000	220
75	2.4383	311	–	–
30	2.4156[*]	311	–	–
42	–	–	2.3851	311
17	–	–	2.2854	222
50[*]	2.0238	400	–	–
93	–	–	1.9795	400
13	1.6508	422	–	–
24	1.5564	511	–	–
13	1.5399[*]	511	–	–
20	–	–	1.5244	511
35[**]	1.4306	440	–	–
100	–	–	1.3996	440
9	–	–	1.1434	444

[*] $Fe_{0.5}Al_{2.33}O_4$.

[**] Coincide with the lines of aluminum and iron.

X-ray phase analysis of the samples subjected to an explosion was performed using monochromatic $CuK_{\alpha 1}$ radiation in the camera "Huber Imaging Plate Guinier Camera."
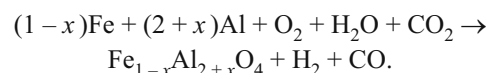
Analysis of the x-ray data presented in Table 2 showed that the explosion acting on sample 1 resulted in the formation of three phases, two of which are iron aluminate with spinel structure and the third is aluminum oxide. Of the iron aluminates, a phase with unit cell parameter $a = 8.090(4)$ Å was present in a large quantity. According the data of [14], this is a solid solution of aluminum oxide with hercynite $Fe_{1-x}Al_{2+x}O_4$. Hercynite with very high degree of inversion

TABLE 3.

I	d_e, Å	hkl	
		variant I	variant II
28	2.8048	022	220
		121	121
78	2.3916	122	221
16	2.2872	220	002
92	1.9816	040	022
		222	040
8	1.8225	114	041
26	1.5250	330	003
100	1.4013	242	123
		151	241
28	1.1837	036	360

of spinel $(Fe_{0.77}Al_{0.23})[Al_{1.77}Fe_{0.23}]O_4$ also possesses a close lattice parameter [24].

During a detonation of any condensed explosive, the hydrogen present in a molecule is virtually completely oxidized to water. Depending on the density of the charge, carbon can either be completely converted into CO_2 or it can be distributed between CO and CO_2. A second variant is possible in charges with a low density. Under the detonation conditions CO_2 and H_2O are active oxidizers of aluminum and iron. Carbon monoxide does not react with aluminum, but it can (according to published data) reduce iron aluminate at temperatures $800 - 1100°C$ to iron according to the reaction

$$FeAl_2O_4 + CO \rightarrow Fe + Al_2O_3 + CO_2.$$

The phase $Fe_{1-x}Al_{2+x}O_4$ can form according to the reaction (4) in which H_2O and CO_2 can participate together with oxygen:

$$(1-x)Fe + (2+x)Al + O_2 + H_2O + CO_2 \rightarrow$$
$$Fe_{1-x}Al_{2+x}O_4 + H_2 + CO.$$

The formation of hercynite with a high degree of inversion is possible according to the reaction (3).

A second phase of iron aluminate was present in a small amount — the x-ray diffraction pattern contained the two weakest lines of spinel with hkl 311 and 511 (they are marked by an asterisk in Table 2). These lines were used to calculate the unit cell parameter: $a = 8.002(2)$ Å. This value differs very little from the one presented in [25] for $Fe_{0.5}Al_{2.33}O_4$ and is the same as the parameter a of the phases $Zn_{0.54}Al_{2.31}O_4$ and $Zn_{0.33}Al_{2.45}O_4$ [27]. Evidently, the phase $Fe_{0.5}Al_{2.33}O_4$ is the product of thermal decomposition of $Fe_{1-x}Al_{2+x}O_4$ or $(Fe_{0.77}Al_{0.23})[Al_{1.77}Fe_{0.23}]O_4$ according to the reaction (5).

The x-ray diffraction pattern of the third phase, which we refer to aluminum oxide, can formally be indexed in the spinel lattice with a high unit cell parameter — $a = 7.920(1)$ Å.

The x-ray diffraction data for sample 2, with the exception of two lines with low intensity (1.8225 and 1.1837 Å), can also be indexed in the spinel lattice but with an even larger parameter a — 7.926(2) Å. The x-ray diffraction patterns of these samples 3, 4, and 5 can be indexed in the spinel lattice with $a = 7.933(3)$, 7.929(3), and 7.934(2) Å, respectively. The ratio of the intensities of the lines of these phases differs from those of σ-Al_2O_3 [5], and with respect to the parameter a it differs from γ-Al_2O_3. We were able to index completely the x-ray diffraction pattern of sample 2 (Table 3) in a primitive hexagonal cell, derived from a cubic face-centered cell with $a = 9.151(1)$ Å, $c = 2c_o = 7.945(2)$ Å (c_o is the parameter of a subcell, equal to 3.972 Å), $c/a = 0.868$, $V = 576$ Å^3. The possible Fedorov groups are $P\frac{6}{m}cc$ and $P6cc$. This hexagonal cell is conjugated to be primitive tetragonal cell with half the volume: $a = 7.941(2)$ Å, $c = 4.575(1)$ Å, $c/a = 0.576$, $V = 288$ Å^3. All lines of the

x-ray diffraction pattern of the aluminum oxide synthesized are completely indexed in the parameters of this cell, just as in the case of the hexagonal cell (see Table 3). In the tetragonal cell, just as in the hexagonal cell, a subcell with the following parameters can be identified: $a_o = a/2 = 3.964$ Å and $c = 4.575$ Å. All lines of the x-ray diffraction pattern, with the exception of 1.8225 and 1.1837 Å, can be indexed in these parameters.

It is impossible to transfer directly from any tetragonal to a hexagonal lattice, with the exception of a variant where the parameter ratio c/a in both lattices equals or is close to 1. This variant occurs in the present work. The matrix of the transformation of the vectors of a tetragonal cell to a hexagonal cell has the form

$$\begin{vmatrix} 0 & 0 & -2 \\ -1 & 0 & 1 \\ 0 & 1 & 0 \end{vmatrix}.$$

The transition from a hexagonal cell into a tetragonal cell is described by the following matrix:

$$\begin{vmatrix} -0.5 & 0.5 & 0 \\ 0 & 0 & 1 \\ -0.5 & -0.5 & 0 \end{vmatrix}.$$

A similar case was observed in [30], where the mechanism of the transformation of the structure of the type observed in high-temperature quartz into a structure of the type observed in keatite was examined in the compound $LaAlSi_2O_6$. This compound has two polymorphic modifications. One of them is obtained by heating glass with spodumene composition $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$ and has a structure of the type observed in high-temperature quartz with $a = 5.217$ Å, $c = 5.464$ Å, $c/a = 1.047$, $V = 128.8$ Å³. The second modification is formed on heating and possesses the structure of keatite with a tetragonal lattice: $a = 7.541$ Å and $c = 9.156$ Å, $c/a = 1.214$, $V = 520.7$ Å³. The transition from a tetragonal to a hexagonal lattice with $a = 5.298$ Å, $c = 5.332$ Å, $V = 129.6$ Å³ can be accomplished with the matrix

$$\begin{vmatrix} 0.25 & 0.25 & 0.25 \\ 0.25 & 0.25 & -0.25 \\ 0.25 & -0.25 & 0.00 \end{vmatrix}.$$

In Table 3 the interplanar distances of the aluminum oxide synthesized are indexed in two variants: in the parameters of a hexagonal lattice (variant I) and a tetragonal lattice (variant II). The indexing and tables 2 and 4 is performed in the spinel lattice. The results of indexing in the two variants are presented in Table 5. If it is assumed that the composition of the synthesized oxide is close to $Al_{8/3}O_4$, then for a hexagonal lattice $Z = 9$ the computed density is 3.527 g/cm³. The

TABLE 4.

Sample 3		Sample 4		Sample 5		hkl
I	d_e, Å	I	d_e, Å	I	d_e, Å	
10	2.8022	10	2.8002	10	2.8024	220
8	2.3941	7	2.3928	9	2.3940	311
9	1.9830	5	1.9825	7	1.9844	400
2	1.5272	2	1.5255	2	1.5270	511
8	1.4021	6	1.4020	7	1.4023	440

TABLE 5.

Sample	Unit cell parameters, Å			
	hexagonal		tetragonal	
	a	c	a	c
1	9.145(3)	7.921(2)	7.916(3)	4.572(2)
2	9.151(1)	7.945(2)	7.941(3)	4.575(3)
3	9.161(5)	7.926(5)	7.931(1)	4.789(2)
4	9.155(5)	7.936(5)	7.929(4)	4.781(6)
5	9.161(5)	7.934(5)	7.933(3)	4.787(4)

absence of single-crystal data does not permit making a unique choice between these lattices and to determine the type of superstructure.

In summary, we have been able to synthesize for the first time the cation-defective iron aluminate $Fe_{0.5}Al_{2.33}O_4$ and a new modification of aluminum oxide under the impact from explosives containing aluminum.

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